

Rheological characterization of geopolymer binder modified by organic resins

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Abstract. The purpose of this study is going to investigate properties of alkali-activated powder (calcined kaolinitic clay and granulated blast furnace slag) prepared as a geopolymer paste and modified by various amount of organic resin. Hybrid organic-inorganic binders were prepared as a mix of organic resin and geopolymer inorganic paste under vacuum conditions. The process of solidification was investigated by measurements of storage (G') and loss modulus (G'') in torsion. The measurement was conducted in oscillatory mode by constant strain of 0.01 %. This strain is set in linear visco-elastic region for minimization influence of paste structure. The effect of organic resin is presented and determined by changes of viscosity (η^*), modules in torsion and tangent of loss angle ($\tan \delta$). Results indicate that addition of organic resin significantly affects the initial viscosity and hardening kinetics.

1. Introduction

Geopolymers are a class of amorphous threedimensional aluminosilicate binder materials, synthesized by reaction of an aluminosilicate powder with a concentrated alkali metal silicate or hydroxide solution [1]. The exchange of silicon for aluminium in the polymer structure results in a net negative charge which is compensated by alkali cations. Geopolymers are generally prepared by mixing of an aluminosilicate raw material in form of a powder with an alkaline silicate solution followed by curing. The most common starting materials are metakaolinite and fly ash, although other aluminosilicate sources such as synthetic aluminosilicate powders and slags are also used [2].

Geopolymers have drawn attention because of their excellent mechanical properties, similar to those offered by the traditional Ordinary Portland Cement (OPC). Applications of geopolymer-based materials in the fields of new ceramics, binders, matrices for hazardous waste stabilization, fire-resistant materials, asbestos-free materials, and high-tech materials have been documented. These materials show excellent mechanical properties, low shrinkage, thermal stability, freeze-thaw, acid and fire resistance, long term durability and recyclability, so the application of geopolymer-based materials covers many fields. On the other hand geopolymers are ceramic materials, so they present a typical brittle mechanical behavior with the consequent low ductility and low fracture toughness. This behavior may represent a great limit in several structural applications. The development of hybrid materials represents a highly interesting and relevant research field for the potentially useful physical properties that could derive from the interfacial interactions of two chemically incompatible phases [3] [4] [5].

Rheology is the study of the fluidity and deformation of matter. The understanding of the rheological properties of cement pastes, mortars and concretes is requisite to ascertaining their consistency and workability and consequently their ease of casting or placement [6] [7] [8] [9].

The main aim of this study is to investigate the rheological properties of hybrid organic-inorganic binders using polyester and epoxy resin. The process of solidification was investigated by measurements of storage and loss modulus in torsion and complex viscosity.



2. Experimental

2.1. Materials

Materials was purchased as commercial product from Ceske lupkove zavody, a.s. (Czech Republic) as two component geopolymeric binder based on fired clays (SiO_2 - 47.4%, Al_2O_3 - 29.7%, CaO - 14.5%, MgO - 3.5%, TiO_2 - 1.8%, Fe_2O_3 - 0.8%, K_2O - 0.5%, Na_2O - 0.1%) activated with potassium silicate solution.

The epoxy (CHS-EPOXY 324) and polyester (Polyester 109) resin was purchased from Sincolor Company. Hybrid composites with epoxy resin (EPO) and polyester resin (PES) were prepared incorporating the resin into the geopolymeric matrix suspension under vacuum stirring, when both polymerization reactions have not been completed yet. Epoxy and polyester resins were obtained by mixing their components in weight ratio as specified in the technical data sheet supplied by the manufacturer.

2.2. Methods

Rheological analyses were performed by ARES G2 rheometer (TA Instrument). The measurement was conducted in oscillatory mode by constant strain of 0.01%. The conditions of measurement were as follows. Radial velocity 1 rad/sec and strain 0.01% were applied to ensure a minimal influence on the hardening process. The effect of organic resins is presented and determined by changes of complex viscosity (η^*), modules in torsion and tangent of loss angle ($\tan \delta$).

SEM analysis was carried out by means of a NeoScope JCM-5000 microscope (JEOL). Micrographs showed obtained from fracture surfaces of hybrid pastes EPO 0-15 % and PES 0-15 %.

3. Results and Discussion

3.1. GEO-EPO hybrid pastes

Figure 1. shows the complex viscosity versus time for the samples EPO 0-15%. The value of the initial complex viscosity pastes without resin were 1000 Pa . s and increase of viscosity begins at 3000 s. The initial complex viscosity of pastes with epoxy resin were 100 Pa . s. The time when the viscosity began to increase was shortened with the amount of resin. Increase of viscosity began at 2000 s for pastes with 1% of epoxy resin and 300 s for pastes with a 15 % resin.

Figure 2. shows changes of loss angle with time. Table 1. shows these changes and it is evaluated as "transition point" - the time when there was a significant change in the properties examined pastes. This point can be considered as transition of inner structure from pseudoliquid solution to inorganic polymer network.

Figure 3. shows micrographs obtained from fracture surfaces of hybrid pastes EPO 0-15%.

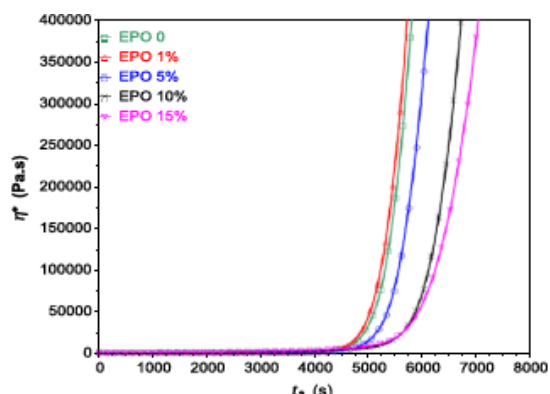


Figure 1. Complex viscosity versus time for samples EPO 0, 1, 5, 10 and 15 %

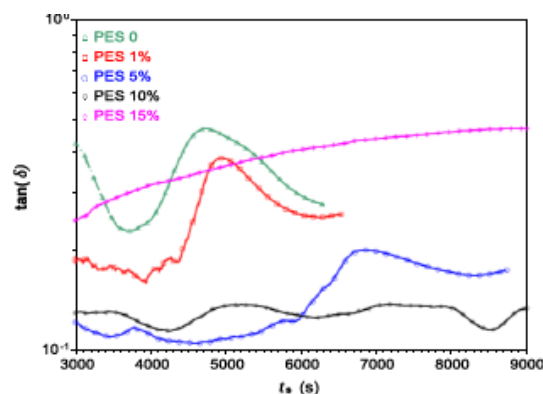


Figure 2. Changes of loss angle with time for samples EPO 0, 1, 5, 10 and 15%

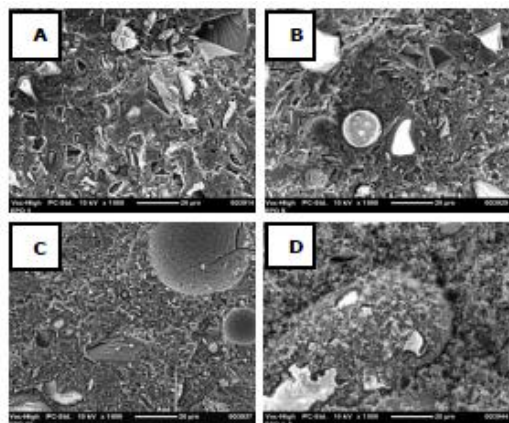


Figure 3. Scanning electron microscope (SEM) micrographs of (A, B, C, D) EPO 1-15 %

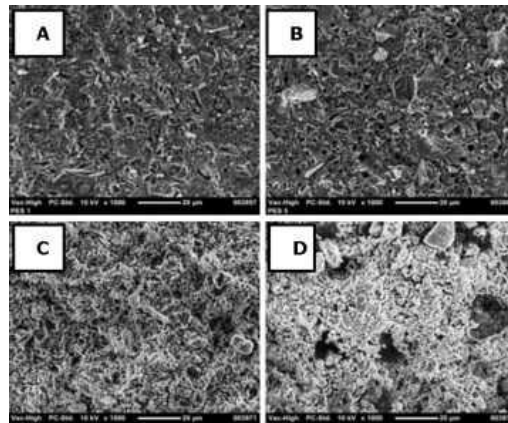


Figure 4. Scanning electron microscope (SEM) micrographs of (A, B, C, D) PES 1-15%

Table 1. Transition point - changes of loss angle with time

Sample	EPO %	0 EPO 1 %	EPO 5 %	EPO 10 %	EPO 15 %
Transition point (s) *	4676	4647	4981	5574	5630

* transition point of polycondensation reaction of geopolymer

3.2. GEO-PES hybrid pastes

Figure 5. shows the complex viscosity versus time for the samples PES 0-15%. The value of the initial complex viscosity pastes without resin were 1000 Pa. s and increase of viscosity begins at 3000 s. The initial complex viscosity of pastes with polyester resin were 100 Pa. s (PES 1%) and 2000 Pa 's (PES 5-15%). The time when the viscosity began to increase was shortened with the amount of resin. Increase of viscosity began at 300 s for pastes with polyester resin (5-15%).

Figure 6. shows changes of loss angle with time. Table 2 shows these changes and it is evaluated as "transition point" - the time when there is a significant change in the properties examined pastes. This point can be considered as transition of inner structure from pseudoliquid solution to inorganic polymer network.

Figure 4. shows micrographs obtained from fracture surfaces of hybrid pastes PES 0-15%

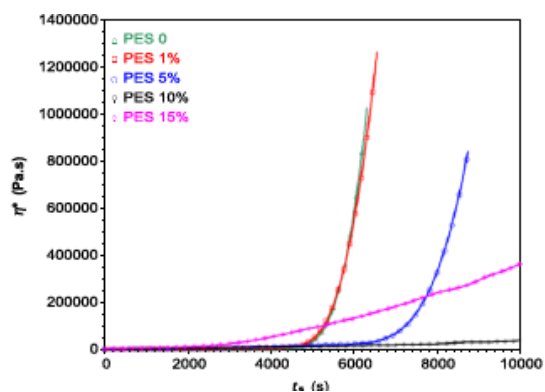


Figure 5. Complex viscosity versus time for samples PES 0, 1, 5, 10 and 15 %.

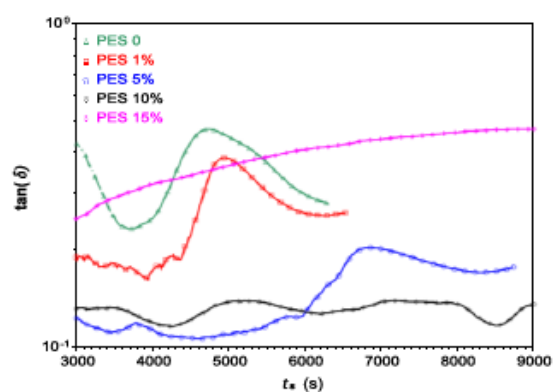


Figure 6. Changes of loss angle with time for samples PES 0, 1, 5, 10 and 15 %.

Table 2. Transition point - changes of loss angle with time

Sample	PES 0%	PES 1%	PES 5%	PES 10%	PES 15%
Transition point (s) *	4676	4958	6989	-	-

* transition point of polycondensation reaction of geopolymer

4. Conclusions

Series of alkali-activated geopolymer composites, incorporated with different amount of resin were synthesized. The effect of organic resin is presented and determined by changes of viscosity, modules in torsion and tangent of loss angle. The complex viscosity and tangent of loss angle appeared to be influenced by concentration of organic resin: when it increases the kinetic of geopolymerisation decreases. This influence is particularly apparent at higher concentrations of organic resins (10 and 15%).

The rheological properties of geopolymer hybrid pastes with polyester resin at concentrations of 10 and 15 % showed a significant deviation. These geopolymer hybrid pastes were poorly workable, they had significantly prolonged curing time (over 14 days) and poor cohesion. In this type of resin would seem appropriate initial compatibilization with the matrix in order to improve the connection of these two phases.

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